

# Effect of Electron Beam Radiation on Structural Changes of Trimethylol Propane Trimethacrylate, Ethylene Vinyl Acetate, and Their Blends

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## SYNOPSIS

The effect of electron beam irradiation at different radiation doses (2, 5, 10, 15, and 20 Mrad) on trimethylol propane trimethacrylate (TMPTMA), ethylene vinyl acetate (EVA, 12% vinyl acetate content), and their blends (0.5, 1, 1.5, 2, 2.5, 3, and 5 parts/100 parts EVA) was investigated. An IR study showed some residual unsaturations retained in irradiated pure TMPTMA, while in blends all unsaturations were used up at a very early stage of irradiation. The concentration of the carbonyl group due to air oxidation increased in pure EVA and blends, but it reached a maximum at the 1.5-part TMPTMA level and 5-Mrad dose. Some ether linkages were formed during irradiation in pure EVA and the blends, although in pure EVA the concentration of ether linkages reached a maximum at the 2-Mrad dose and then decreased and in the blends it increased with an increase in radiation dose. Gel content showed an increasing trend with an increase in radiation dose, but it increased marginally with TMPTMA level. A blend of EVA with 1 part TMPTMA produced more gel than pure EVA at the same irradiation dose. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Modification of polymers in the presence of radiation is a potential method for development of new polymers and composites. Use of some polyfunctional monomers in such a reaction is very effective in decreasing the dose level to achieve the optimum properties without much deterioration of the base polymer.

Polyethylene and its blends<sup>1-3</sup> and poly(vinyl chloride) (PVC)<sup>4,5</sup> were modified using various multifunctional monomers by electron beam radiation.

Ethylene vinyl acetate (EVA) is a copolymer composed of ethylene and vinyl acetate. It is a good insulating material for high voltage cables. The effect of irradiation on trimethylol propane trimethacrylate (TMPTMA), which is used as a radiation sensitizer, EVA copolymer, and a mixture of EVA and TMPTMA has not been reported so far.

In principle, any polyfunctional unsaturated monomer is capable of promoting irradiation crosslinking of EVA. The most effective compound in crosslinking of polymers are polyfunctional acrylates and methacrylates, especially trifunctional monomers such as TMPTMA. These monomers are particularly efficient because they produce high yield of radicals during irradiation.<sup>4-10</sup> In this study structural changes of TMPTMA, EVA, and blends of EVA with TMPTMA due to irradiation were investigated by infrared (IR) spectroscopy.

## EXPERIMENTAL

### Materials

PILENE EVA (12% VA content, density 0.940 g/cm<sup>3</sup>, melt index 0.2–0.4 dg/min) was supplied by Polyolefin Industries Ltd., Bombay, India.

TMPTMA was obtained from ANCOMER Ltd., England.

EVA was mixed with TMPTMA in a Brabender Plasticorder PLE-651 at 120°C and 60 rpm rotor

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**Table I Formulations of Samples**

Sample Code	EVA (Wt by Parts)	TMPTMA Level (Wt by Parts)	Radiation Dose (Mrad)
ETM-12/0.5/5	100	0.5	5
ETM-12/1/5	100	1.0	5
ETM-12/1.5/5	100	1.5	5
ETM-12/2/5	100	2.0	5
ETM-12/2.5/5	100	2.5	5
ETM-12/3/5	100	3.0	5
ETM-12/5/5	100	5.0	5
ETM-12/1/2	100	1.0	2
ETM-12/1/10	100	1.0	10
ETM-12/1/15	100	1.0	15
ETM-12/1/20	100	1.0	20

speed. The mixes were compression molded between aluminum foils at 120°C and 13-MPa pressure in an electrically heated press.

The molded EVA samples, in the form of rectangular sheets, and TMPTMA were irradiated by an electron beam accelerator (model ILU-6) at Bhabha Atomic Research Centre, Bombay. Irradiation doses of 2, 5, 10, 15, and 20 Mrad were used. The formulations of samples and specifications of the electron beam accelerator are given in Tables I and II, respectively.

### IR Spectra

IR spectra of blends of EVA with different parts of TMPTMA were taken on melt pressed thin films (100 μm) and IR spectra of TMPTMA samples were taken on KBr (potassium bromide) pellets using a Perkin-Elmer (model 837) spectrophotometer. The area under the peak and absorbances at different frequencies were obtained from standard Perkin-Elmer software (IR Data Manager, Version 2.50) after baseline correction. All the results given in this article are the average of three measurements.

### Gel Fraction

Gel fraction was measured gravimetrically by immersing the samples in xylene at 80°C for 72 h.

## RESULTS AND DISCUSSION

Figure 1(a) describes the IR spectra of pure TMPTMA in the region of 2000–1100 cm<sup>-1</sup>. The peak positions and their respective assignments

are given in Table III. These peaks are in good agreement with the literature values<sup>11</sup> and can be explained from the structure of TMPTMA shown below.

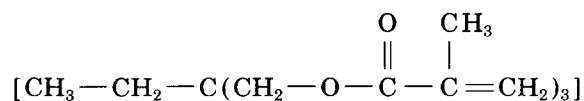
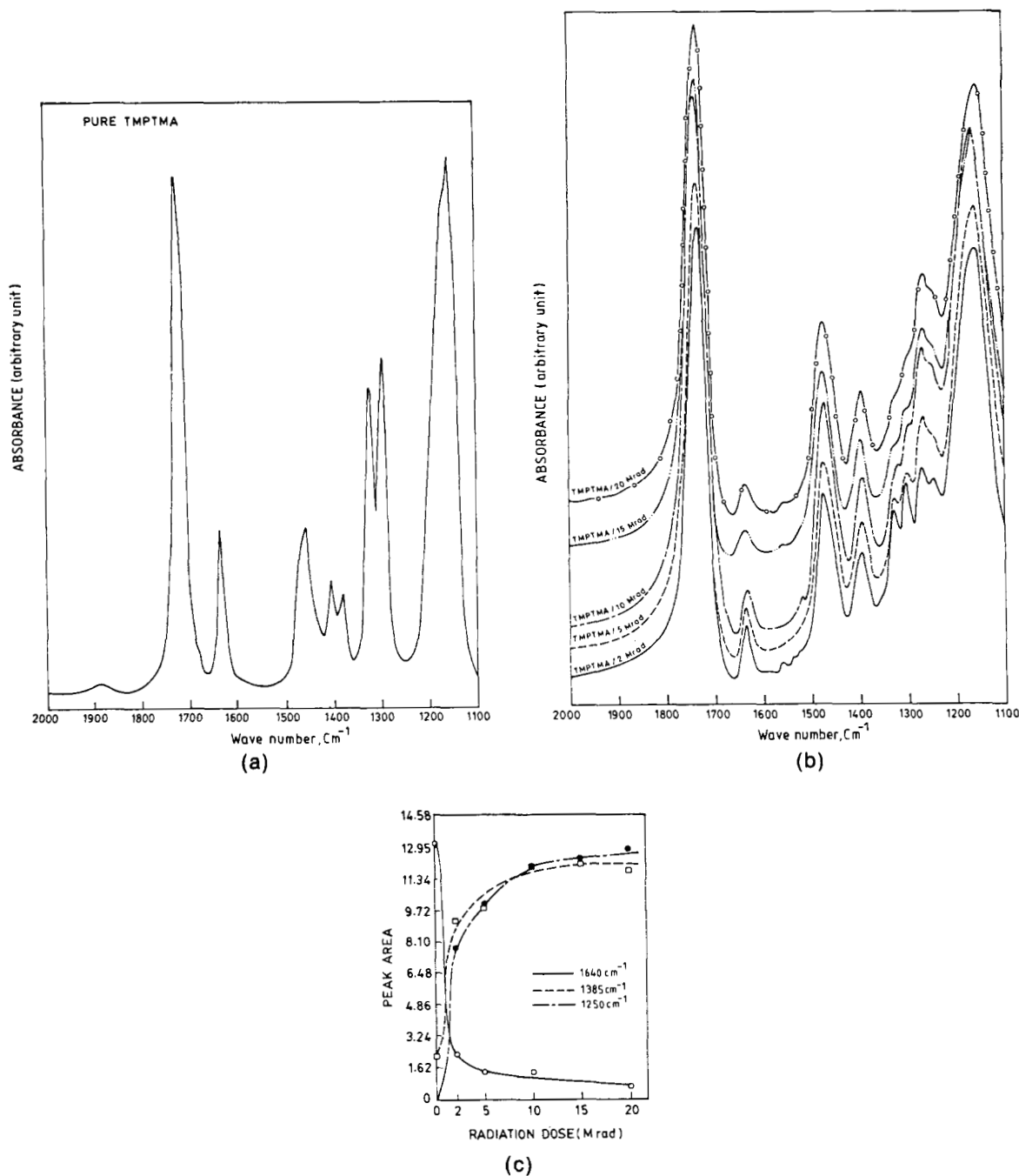


Figure 1(b) shows the IR spectra in the 2000–1100 cm<sup>-1</sup> region of irradiated TMPTMA with radiation doses of 2, 5, 10, 15, and 20 Mrad. From this figure, a gradual decrease of peak intensity at 1637, 1298, and 1323 cm<sup>-1</sup> due to  $\text{>C}=\text{C}<$ , disubstituted alkene, and C—H in plane deformation of the —CH=CH<sub>2</sub> group, respectively, is observed with an increase in irradiation dose. Disappearance of the peak at 1406 cm<sup>-1</sup> is also observed as TMPTMA is irradiated with a 2-Mrad irradiation dose. The changes of the area under the band at 1637 cm<sup>-1</sup> due to  $\text{>C}=\text{C}<$  stretching with the radiation dose is shown in Figure 1(c). The peak area decreases sharply at the 2-Mrad dose. The decrease is marginal after the critical dose. The above observations can be explained as follows.

TMPTMA polymerizes by radiation through unsaturation (Scheme 1) and forms a network structure by crosslinking. As a result, it transforms from the liquid to solid state. All the residual unsaturation observed in the crosslinked material must be due to unreacted double bonds. The restricted mobility of

**Table II Specification of Electron Beam Accelerator (ILU-6)**

Energy range	0.5–2.0 MeV
Beam power through whole energy range	20 kW
Beam energy spread	±10%
Average current (E-1.5 MeV)	15 mA
Adjusting limits for current	0–30 mA
Accelerating voltage frequency	100–120 MHz
Duration of pulse	400–700 μs
Repetition rate	2–50 Hz
Pulse current	
Maximum	900 mA
Minimum	400 mA
Power supply	
Voltage	3 × 380/220 V
Voltage frequency	50 Hz
Total power consumption	150 kW



**Figure 1** IR spectra of (a) pure TMPTMA, (b) pure TMPTMA irradiated with 2, 5, 10, 15, and 20 Mrad, and (c) area under the band at 1640, 1250, and 1385  $\text{cm}^{-1}$  of pure irradiated TMPTMA vs. irradiation dose.

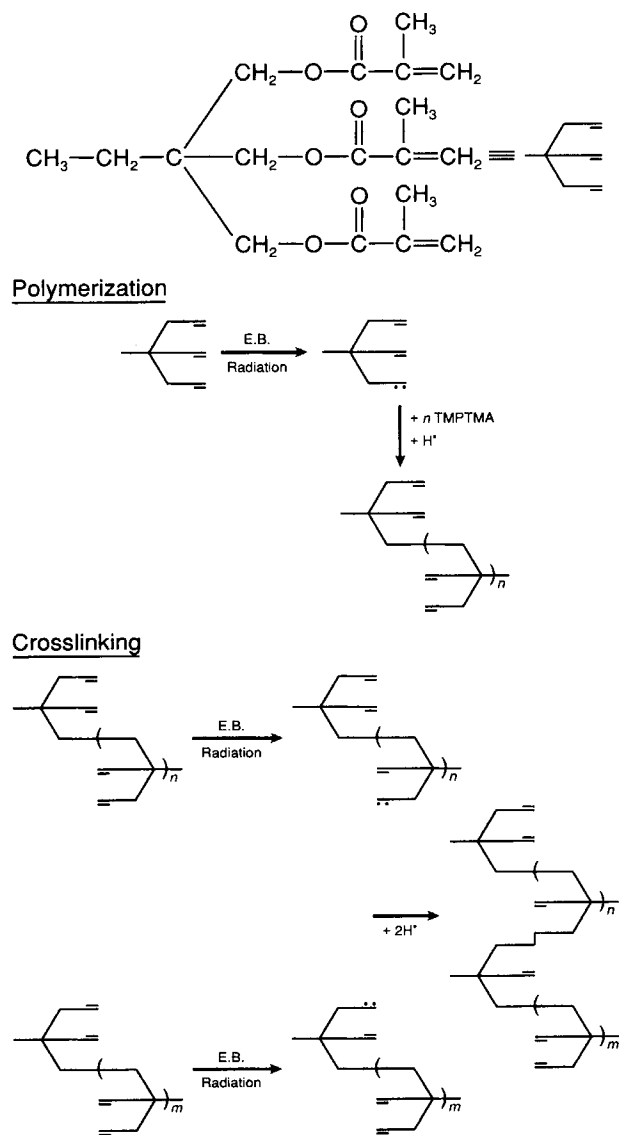
TMPTMA molecules due to its bulky structure shields the double bonds from further reaction in the 3-dimensional TMPTMA network formed during irradiation. Appearance of another peak at 1250  $\text{cm}^{-1}$ , a strong band at 1385  $\text{cm}^{-1}$  due to C—C skeletal vibration of the  $-\text{C}(\text{CH}_3)_3$  group and C—H

deformation vibration of  $-\text{CH}_3$  in the spectra of irradiated TMPTMA, and also the area under the band at 1250 and 1385  $\text{cm}^{-1}$  [Fig. 1(c)] supports the formation of saturated hydrocarbon and  $-\text{CH}_3$  groups on irradiation.

IR spectra of pure EVA in the region of 2000–

**Table III Peak Positions and Assignments for Pure TMPTMA IR Spectra**

Wave Number ( $\text{cm}^{-1}$ )	Groups
1728	$\text{>C=O}$ (carbonyl stretching)
1637	$\text{>C=C<}$ (double bond stretching for vinylidene gr.)
1457	$\text{>CH}_2$ (scissor vibration)
1406	$\text{>CH}_2$ (in plane deformation of vinylidene hydrocarbon)
1383	C—H (deformation vibration of $\text{CH}_3$ )
1323	C—H [in plane deformation of ( $-\text{CH}=\text{CH}_2$ ) gr.]
1298	Disubstituted alkene
1159	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOR}$ gr.

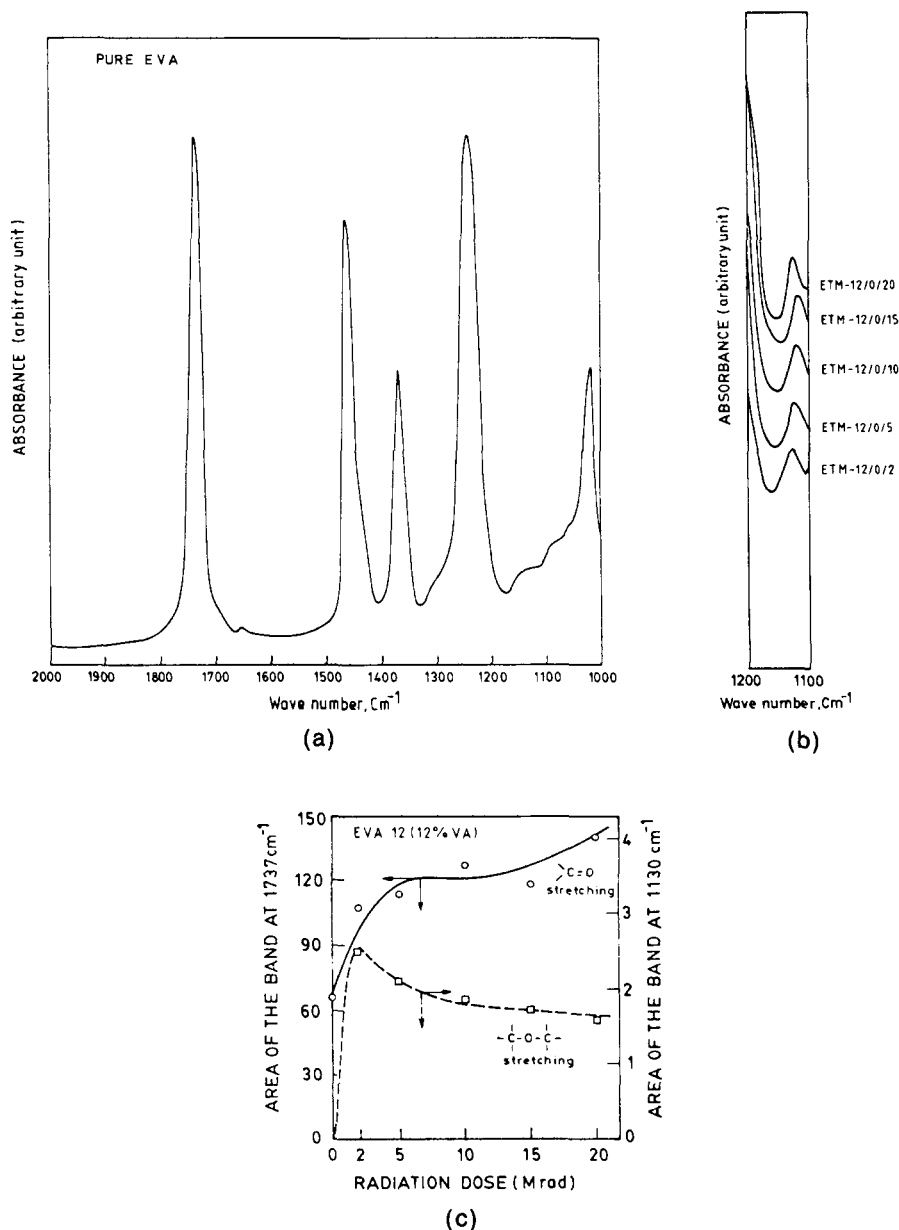
**Scheme 1**

$1000\text{ cm}^{-1}$  is shown in Figure 2(a). Table IV describes the peak positions and respective assignments. These peaks are in good agreement with the literature values.<sup>11</sup> On irradiation with 2, 5, 10, 15, and 20 Mrad doses, the above peaks along with a peak at  $1130\text{ cm}^{-1}$  appear [Fig. 2(b)] due to formation of ether linkage (Scheme 2). Figure 2(c) describes the variation of the area under the bands at  $1740$  and  $1130\text{ cm}^{-1}$  due to  $\text{>C=O}$  stretching

and ether linkage ( $-\text{C}-\text{O}-\text{C}-$ ) with radiation dose. The concentration of the carbonyl group increases with the radiation dose, whereas the concentration of ether linkage increases up to 2 Mrad and then decreases. The air oxidation probably increases with an increase of irradiation dose due to availability of a large number of free radicals leading to an increase in the concentration of the  $\text{>C=O}$

groups (Scheme 2). On the other hand, at higher irradiation dose, various competitive reactions take place in the presence of an enormous amount of free radicals including chain scission, recombination, termination, and disproportionation followed by addition of macroradicals to the  $\pi$  electron (Scheme 3) and due to breaking of the  $\text{C}-\text{O}-\text{C}$  bond. (Bond energy of  $\text{C}-\text{O}$  is less than that of  $\text{C}=\text{O}$ . The value of the former is  $85.5\text{ kcal/mol}$ , that of the latter is  $176\text{--}179\text{ kcal/mol}$  at  $25^\circ\text{C}$ ).<sup>12</sup> The interplay of these reactions and restricted chain mobility due to crosslinking is reflected in the decreasing trend of the concentration of ether linkage as the irradiation dose is increased.

Figure 2(d) shows the IR spectra in the region of  $1500\text{--}1400\text{ cm}^{-1}$  of pure EVA and EVA irradiated with irradiation doses of 2, 5, 10, 15, and 20 Mrad. A sharp peak at  $1470\text{ cm}^{-1}$  is observed in pure EVA



**Figure 2** IR spectra of (a) pure EVA, (b) pure EVA irradiated with 2, 5, 10, 15, and 20 Mrad in the region of 1200–1100 cm<sup>-1</sup>, (c) area under the band at 1740 and 1130 cm<sup>-1</sup> due to  $\text{>C=O}$  and  $\text{-C-O-C-}$  linkages vs. irradiation dose, (d) pure EVA and EVA irradiated with 2, 5, 10, 15, and 20 Mrad and (e) EVA containing different parts of TMPTMA irradiated with a dose of 5 Mrad in the region of 1500–1400 cm<sup>-1</sup>.

due to C—H deformation vibration of the  $\text{>CH}_2$  group; a band at 1450 cm<sup>-1</sup> appears on irradiation. The latter becomes more prominent as irradiation dose is increased. This is due to the formation of a small ring ketone.<sup>11</sup>

As the irradiation dose is increased, the polymer backbone is oxidized (Scheme 2) and breaks down

into small fragments by the free radical mechanism. Cyclization of small fragments containing the  $\text{>C=O}$  group by free radical recombination may result in the formation of a small ring ketone (Scheme 4).

Figure 2(e) represents the IR spectra in the region of 1500–1400 cm<sup>-1</sup> of pure EVA and EVA con-

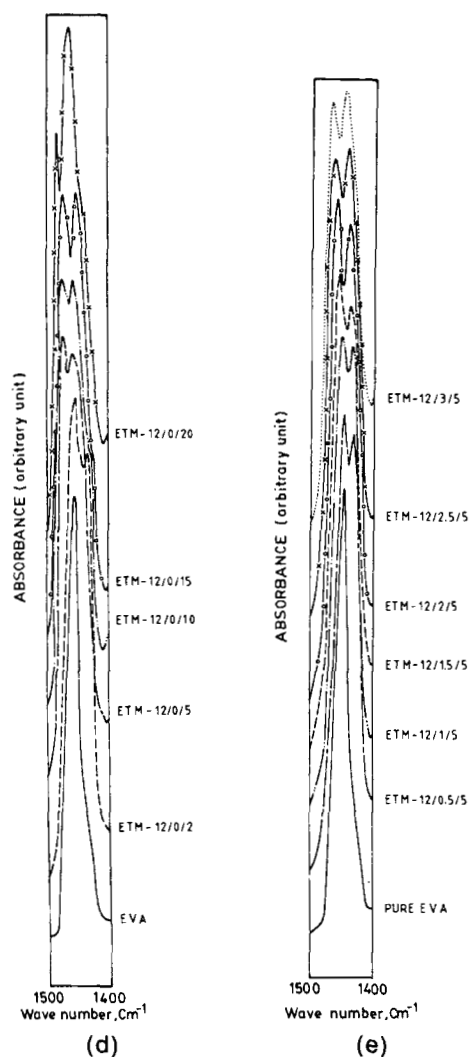


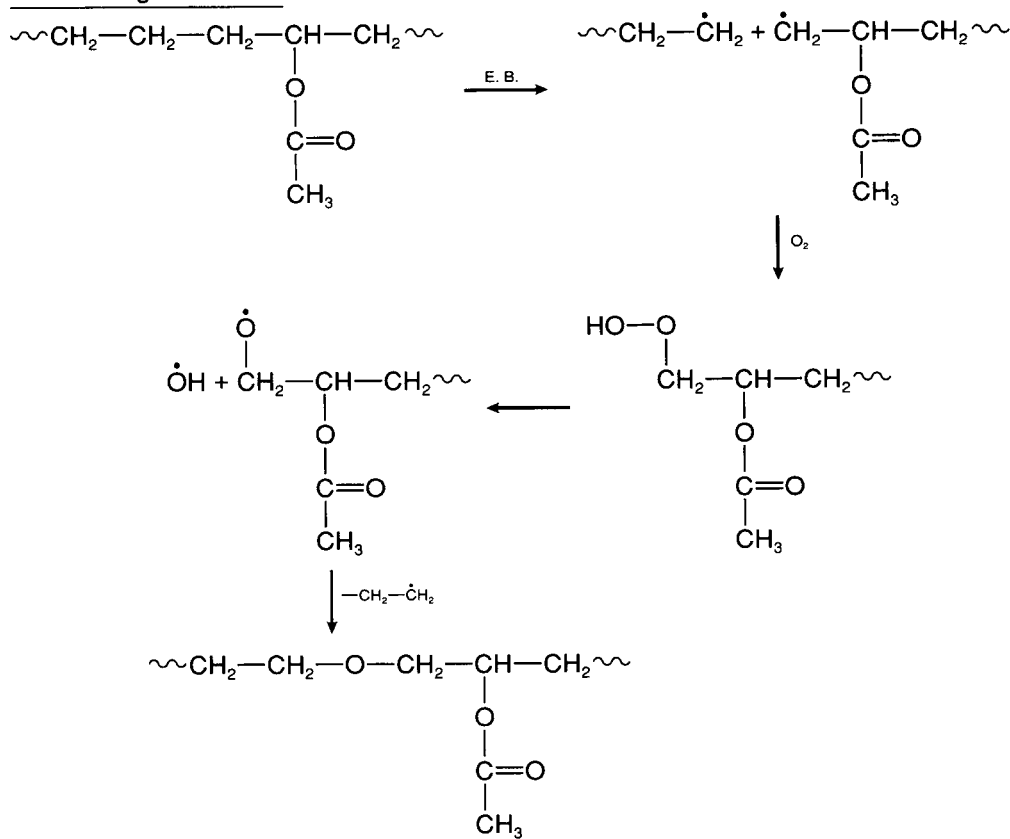
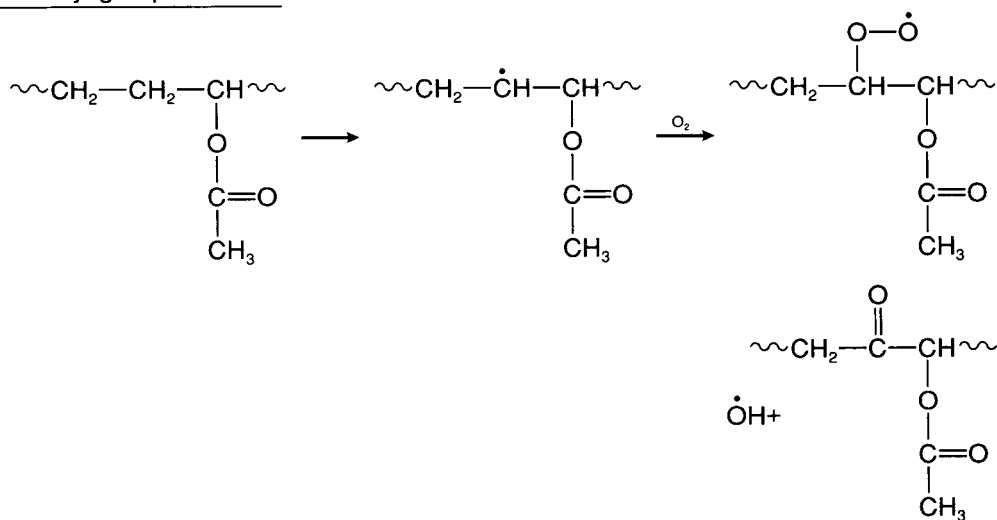
Figure 2 (Continued from the previous page)

taining different parts of TMPTMA (0.5, 1, 1.5, 2, 2.5, and 3 parts by weight), each irradiated with a constant radiation dose of 5 Mrad. As the concentration of TMPTMA increases, the peak at  $1450\text{ cm}^{-1}$  becomes more prominent. As the TMPTMA

level increases, more free radicals are generated during irradiation that are responsible for more oxidation and chain scission. Short chain diradicals containing the ketone group are formed that by recombination produce a small ring ketone.

Table IV Peak Positions and Assignments of Pure EVA IR Spectra

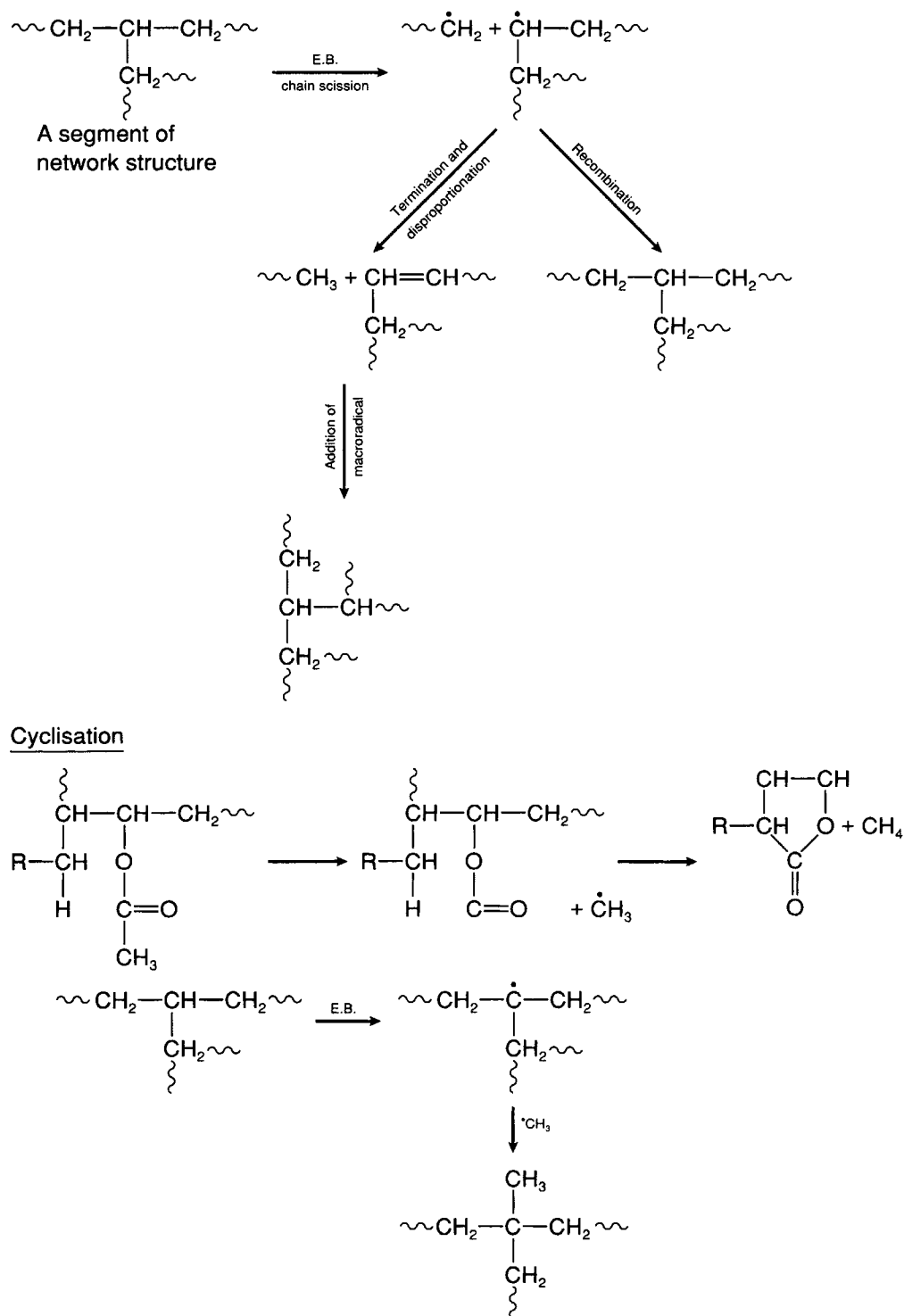
Wave Number ( $\text{cm}^{-1}$ )	Groups
1740	$\text{>C=O}$ (carbonyl stretching for ester group)
1470	$\text{C-H}$ (bending vibration of $\text{CH}_2$ )
1375	$\text{C-H}$ (bending vibration of $\text{CH}_3$ )
1244 and 1030	$\begin{array}{c}   \quad   \\ =\text{C}-\text{O}-\text{C}- \\   \end{array}$ (stretching vibration)

Ether linkage formationCarbonyl group formation

Scheme 2

Figure 3 (a) describes the IR spectra in the region of 2000–1000  $\text{cm}^{-1}$  of pure EVA, EVA containing 5 parts TMPTMA, and EVA containing 5 parts TMPTMA irradiated with a 2-Mrad irradiation dose, respectively.

The spectra of the unirradiated blend of EVA and TMPTMA show a sharp peak at around 1640  $\text{cm}^{-1}$  due to  $\text{>C=C<}$  stretching of mainly *trans*-vinylenes expected from the IR spectra of TMPTMA

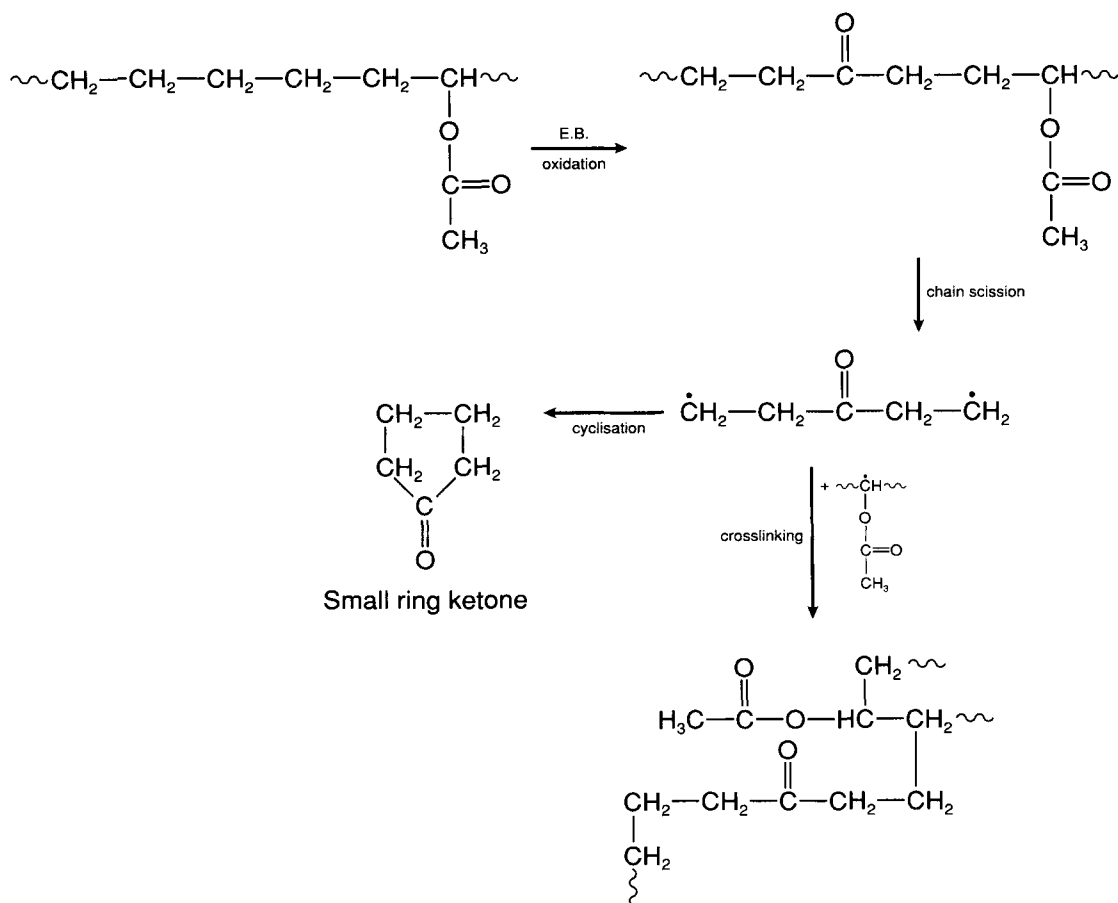


Scheme 3

and EVA [Figs. 1(a), 2(a)]; but as the blend is irradiated with a 2-Mrad dose, the peak at  $1640\text{ cm}^{-1}$  disappears. When pure TMPTMA is irradiated with a 2-Mrad radiation dose, there are some residual

unsaturations, because its crosslinked bulky structure shields the double bonds from further reaction (discussed earlier). But in blends of 5 parts TMPTMA and EVA, the shielding does not take





Scheme 4

place due to homogeneous dispersion of TMPTMA molecules in the polymer matrix and all double bonds are used up. Because no characteristic peak of TMPTMA ( $1640\text{ cm}^{-1}$ ) was found in the ether extract of the irradiated samples containing TMPTMA, it can be concluded that all TMPTMA added in various samples is used for grafting and crosslinking through unsaturation at the early stage of irradiation.

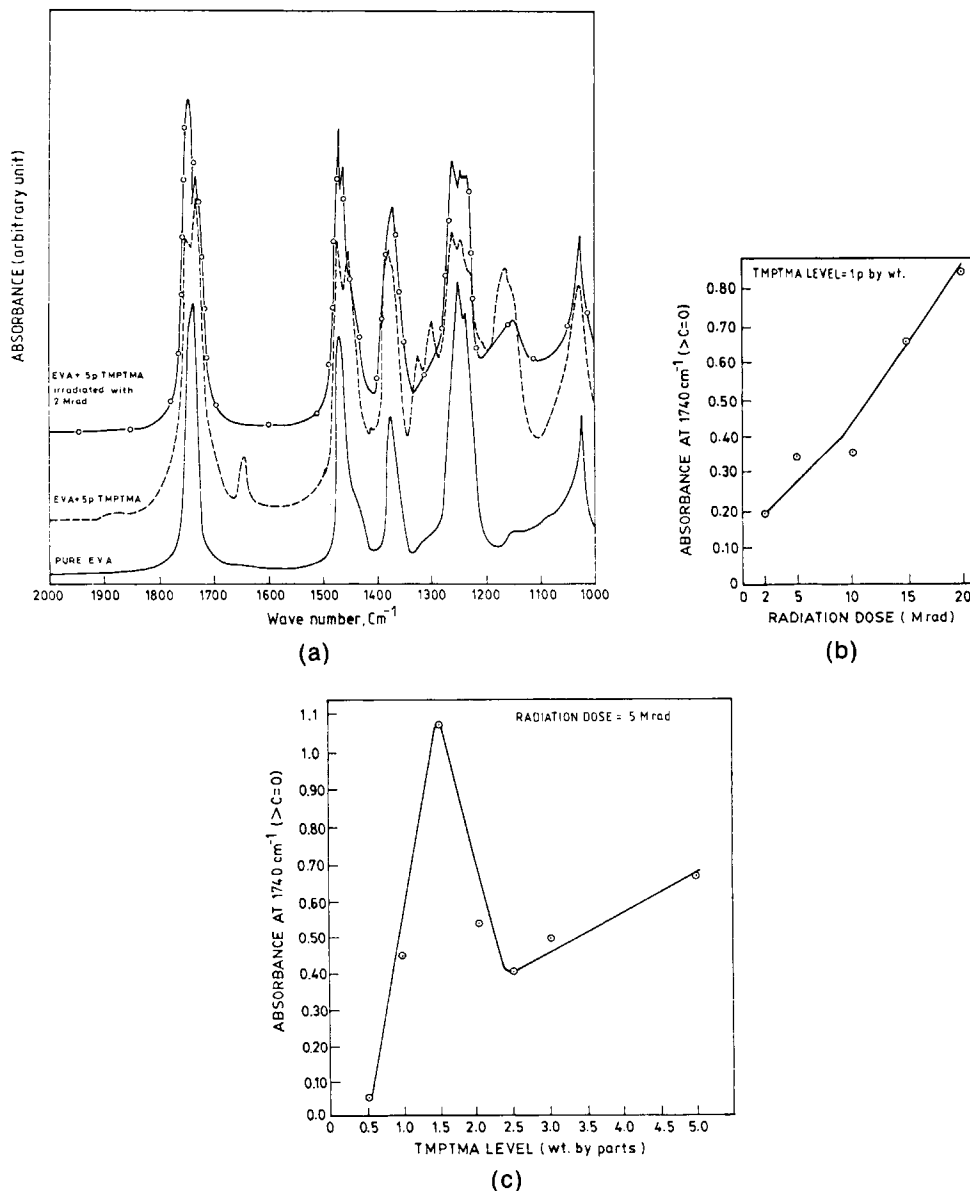
Figure 3(b) and (c) show the variation of absorbance at  $1740\text{ cm}^{-1}$  due to  $\text{>C=O}$  stretching vibration (obtained from the difference spectra of blends and pure EVA) with variation of irradiation dose of samples containing 1 part TMPTMA and a TMPTMA level having a constant irradiation dose of 5 Mrad. Like pure EVA,  $\text{>C=O}$  stretching absorbance [Fig. 2(c)] increases sharply with irradiation dose due to air oxidation of samples during irradiation (Scheme 2). On the other hand, variation

of absorbance with TMPTMA level is rather irregular. Probably the grafting, crosslinking, and oxidation reactions predominate up to 1.5 parts of TMPTMA when  $\text{>C=O}$  concentration increases.

Above the 1.5 parts, chain scission and breakdown of network structure due to availability of a large number of free radicals takes place (Scheme 3). Ultimately oxidation predominates with an increase of TMPTMA level due to the presence of more free radicals produced from TMPTMA.

In Figure 4(a-c) absorbances due to  $\text{>CH}_2$  scissor vibration, C—H bending vibration of  $-\text{CH}_3$ ,  $-\text{C}-\text{O}-\text{C}-$  stretching, and C—O stretching are plotted against irradiation dose for samples having 1 part TMPTMA.

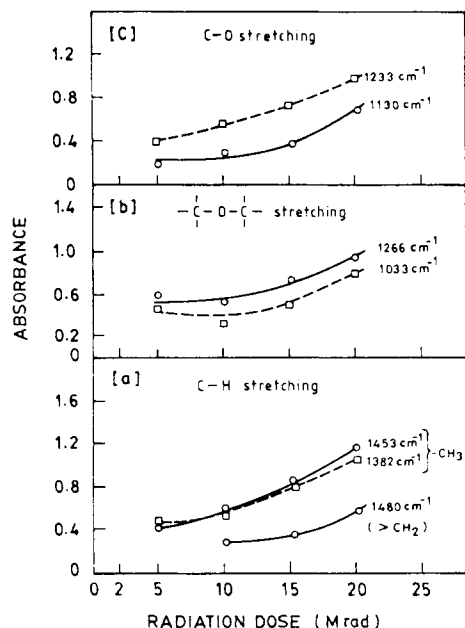
Absorbance due to  $\text{>CH}_2$  scissor vibration remains almost constant with the increase of irradiation dose up to 15 Mrad, then increases marginally



**Figure 3** (a) IR spectra of pure EVA, unirradiated EVA containing 5 parts TMPTMA, and irradiated EVA containing 5 parts TMPTMA with a 2-Mrad radiation dose. Plot of carbonyl ( $>C=O$ ) absorbance of different irradiated samples (b) with variation of irradiation dose containing 1 part TMPTMA and (c) with variation of TMPTMA level having a constant irradiation dose of 5 Mrad.

with irradiation dose. Up to a 15-Mrad dose, there is probably a balance between various reactions (Scheme 3). After 15 Mrad, chain scission, disproportionation, and cyclization reactions probably predominate. Absorbance due to C—H bending vibration of  $—CH_3$  increases with an increase in irradiation dose. This may be due to the predominating tendency of chain scission, termination, and cy-

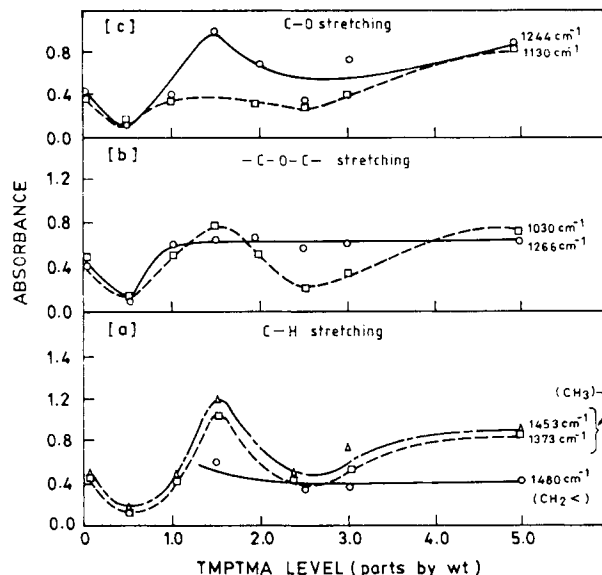
clization at the higher irradiation dose. Variation of absorbance due to  $—C—O—C—$  stretching and C—O stretching shows a similar trend to that in Figure 4(a), but in pure EVA the concentration of ether linkage decreases beyond the 2-Mrad dose. This is probably due to the fact that more ether linkages are formed in the presence of 1 part TMPTMA that produce more free radicals at higher



**Figure 4** Plot of absorbance of (a) C—H stretching vibration of the  $\text{>CH}_2$  and  $\text{-CH}_3$  groups, (b)  $\text{-C-O-C-}$  stretching vibration, and (c) C—O stretching vibration at different frequencies with radiation dose.

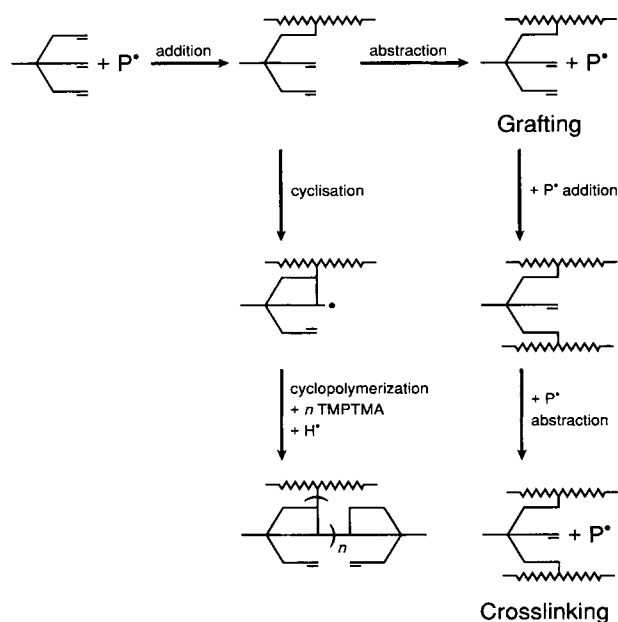
irradiation dose and promotes the chain scission and oxidation by the free radical mechanism (Scheme 2).

Figure 5(a-c) represent the effect of TMPTMA level on the absorbance at the same frequencies mentioned previously. Absorbance due to  $\text{>CH}_2$  scissor vibration remains almost constant over the whole range of TMPTMA levels. This is probably due to a balance between different factors, that is, addition of TMPTMA, chain scission, oxidation of the backbone of EVA, disproportionation, and cyclization reactions (Schemes 2-5). Absorbance due to C—H bending of  $\text{-CH}_3$  increases with increasing TMPTMA level up to 1.5 parts and then decreases before a final increase beyond 2.5 parts. The initial increase of absorbance is due to more available  $\text{-CH}_3$  from TMPTMA. After 1.5 parts, the absorbance decreases, probably due to the predominating tendency of crosslinking, cyclization, and chain scission (Schemes 3-5). Finally it increases due to further oxidation and chain scission due to the presence of a large number of free radicals. The plots of variation of absorbance due to  $\text{-C-O-C-}$  and C—O stretching with TMPTMA level show a trend similar to Fig. 5(a). From these plots it may be con-



**Figure 5** Plot of absorbance of (a) C—H stretching vibration of  $\text{>CH}_2$  group and  $\text{-CH}_3$  group, (b)  $\text{-C-O-C-}$  stretching vibration, and (c) C—O stretching vibration at different frequencies with TMPTMA level.

cluded that some ether linkages due to oxidation and chain scission in the presence of free radicals are produced, which increase with the TMPTMA level up to 1.5 parts. After that the reaction between



**Scheme 5**

free radicals and the matrix takes place predominately. Finally oxidation predominates due to the presence of enormous amounts of free radicals as TMPTMA level is increased.

### Gel Content

The gel content of EVA, EVA containing 1 part TMPTMA irradiated with 2, 5, 10, 15, and 20 Mrad irradiation dose, and EVA containing various levels of TMPTMA (0.5, 1, 1.5, 2, 2.5, 3, and 5 parts) irradiated with a radiation dose of 5 Mrad is plotted against the irradiation dose and the TMPTMA level in Fig. 6(a-c), respectively.

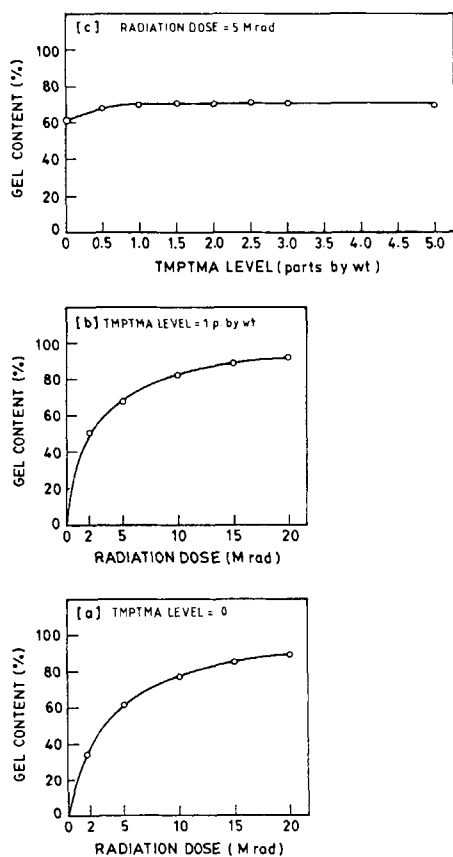
The gel content of pure EVA and EVA containing 1 part TMPTMA increases sharply with irradiation dose up to 10 Mrad. Beyond 10 Mrad the increase is marginal. The increase of gel content with the increased irradiation dose indicates the formation

of a 3-dimensional network structure by crosslinking. On the other hand, at higher irradiation dose, the increase is marginal due to the breakdown of network structure (as discussed in the IR study) along with the formation of a macrogel/microgel. At a particular irradiation dose the sample containing 1 part TMPTMA forms more crosslinks than the samples without TMPTMA [Fig. 6(a,b)] as the gel content shows higher value in the 1-part TMPTMA filled system. TMPTMA enhances the crosslink density during irradiation by producing a large number of free radicals that take part in grafting followed by crosslinking with EVA. At a constant 5-Mrad irradiation dose, the gel content marginally increases with TMPTMA level. This may be due to breakdown of the network structure. At a higher TMPTMA level more free radicals are generated during irradiation that promote breakdown of network structure along with the formation of macrogels/microgels.

### CONCLUSIONS

The effect of electron beam irradiation on pure TMPTMA, pure EVA, and their blends was investigated. The following conclusions were made:

1. Pure TMPTMA is polymerized and crosslinked during irradiation and some residual unsaturations are found due to shielding of double bonds by the crosslinked bulky structure, whereas all double bonds are used up in blends by grafting and crosslinking through unsaturation during irradiation.
2. Concentration of carbonyl groups in pure EVA and blends of TMPTMA with EVA increases with irradiation dose due to air oxidation. The concentration of ether linkages in blends increases with radiation dose. In pure EVA it decreases beyond 2 Mrad due to various competitive reactions at the higher irradiation dose and due to the breaking of ether linkages.
3. Gel content increases with irradiation dose for both pure EVA and blends of EVA with TMPTMA, although higher gel content at a particular irradiation dose is found for the blend of EVA and 1 part TMPTMA. Gel content increases very marginally with TMPTMA level.
4. In blends of EVA and TMPTMA, TMPTMA acts as a radiation sensitizer that promotes crosslinking. But a higher radiation dose and



**Figure 6** Variation of percent gel content of (a) pure irradiated EVA with the change of radiation dose, (b) irradiated EVA containing 1 part TMPTMA by wt./100 parts of EVA with radiation dose, and (c) EVA containing different parts of TMPTMA irradiated with 5-Mrad dose with TMPTMA level.

TMPTMA level may cause the degradation of the polymer by oxidation and chain scission.

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